# PATENT ABSTRACTS OF JAPAN

(11)Publication number:

2000-346946

(43) Date of publication of application: 15.12.2000

(51)Int.CI.

G01T 1/04

(21)Application number: 2000-043132

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(22)Date of filing:

21.02.2000

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(30)Priority

Priority number: 11091072

Priority date: 31.03.1999

Priority country: JP

#### (54) INDICATOR SHEET FOR HISTORY OF RADIATION DOSE

(57)Abstract:

PROBLEM TO BE SOLVED: To make easily and accurately displayable the radiation dose by providing a discolored layer where a coloring electron-donor organic compound and an active species generation organic compound contain a hydrophilic compound and a radiation sensitizer on the surface of a base sheet.

SOLUTION: The disoclored layer 1 where a coloring electrondonor organic compound and an active species generation organic compound for coloring the electron donor organic compound contain a hydrophilic compound, and a radiation sensitizer is provided at least one portion of the surface of a base sheet 2. A coloring matter 3 that is approximated to hue before or after the discoloration of the discolored layer 1 may be provided at one portion on the discolored layer 1. Triphenylphthalide, fluorene, phenothiazine, or the like are used

for the coloring electron-donor organic compound, and carbon tetrabromide, tribromoethanol, tribromomethyphenylsulfone, or the like are used for the active species generation organic compound. A macromolecule, an organic low-molecule

compound, anion/cation surface-active agents, or the like are used for a hydrophilic compound.

**LEGAL STATUS** 

[Date of request for examination]

28.06.2002

[Date of sending the examiner's decision of

02.06.2005

rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

' [Date of final disposal for application]

[Patent number] 3732704
[Date of registration] 21.10.2005
[Number of appeal against examiner's decision of 2005-12588

rejection]

[Date of requesting appeal against examiner's 04.07.2005

decision of rejection]

[Date of extinction of right]

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#### **CLAIMS**

## [Claim(s)]

[Claim 1] The radiation dose hysteresis indicator sheet which has the discoloration layer in which the electron donor organic compound of coloration nature and the active species generation organic compound to which coloration of this electron donor organic compound is carried out with a radiation come to contain a hydrophilic compound and a radiosensitizing agent on a part of front face [ at least ] of a base material sheet.

[Claim 2] The amount hysteresis indicator sheet of radiation irradiation according to claim 1 characterized by having coloring matter approximated to the hue before discoloration of a discoloration layer, and after discoloration at the part on said discoloration layer.

[Claim 3] The amount hysteresis indicator sheet of radiation irradiation according to claim 1 with which said discoloration layer is characterized by being covered with transparence or a translucent protection film layer.

[Claim 4] The amount hysteresis indicator sheet of radiation irradiation according to claim 3 characterized by having coloring matter approximated to the hue before discoloration of said discoloration layer, and after discoloration in a part of one field of said protection film layers.

[Claim 5] The amount hysteresis indicator sheet of radiation irradiation according to claim 1 which said base material sheet is transparence or a translucent protection film sheet, and is characterized by giving the adhesive layer to the non-observing field of this protection film sheet.

[Claim 6] The amount hysteresis indicator sheet of radiation irradiation according to claim 5 characterized by giving the coloring matter approximated to the hue before discoloration of said discoloration layer, and after discoloration to a part of one field of said protection film sheets.

[Claim 7] The amount hysteresis indicator sheet of radiation irradiation according to claim 6 characterized by another base material sheet having pasted said adhesive layer.

[Claim 8] The amount hysteresis indicator sheet of radiation irradiation according to claim 1 to 7 characterized by giving the adhesive layer to the non-observing field of said base material sheet.

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#### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the indicator sheet which the dose which irradiated a medical device, transfusion blood, etc. is displayed by change of a color, and the color which changed can recognize clearly, and does not fade.

[0002]

[Description of the Prior Art] Radiation treatment, such as an X-ray and a gamma ray, is performed for sterilization of a medical device, onset prevention of graft versus host disease (TA-GVHD) by transfusion blood, etc. In order to investigate whether the radiation of an initial complement was irradiated by the irradiated object generally, it is carrying out by making the indicator containing the matter discolored irreversibly intermingled between irradiated objects, taking out after radiation irradiation, and checking the discoloration with a radiation.

[0003] These people have applied for the indicator which can already display the wide range exposure to about 25,000Gy of a lot of exposures from about 15Gy of the little exposure to transfusion blood to a medical supply as Japanese Patent Application No. No. 306475 [ten to]. Although this indicator is clear in change of the hue before and behind radiation irradiation and the amount of radiation irradiation could be checked simple and exactly, since it faded gradually after discoloration, an indicator was not able to be saved for a long period of time with the hue after discoloration. Photography etc. needed to be performed in order to record the hue after discoloration.

[0004]

[Problem(s) to be Solved by the Invention] It was made in order that this invention might solve the aforementioned technical problem, and it aims at offering the indicator sheet which does not fade even if it can display the amount of radiation irradiation simple and exactly by clear change of a hue and saves it for a long period of time.

[0005]

[Means for Solving the Problem] It is as follows when the drawing corresponding to an example explains the amount hysteresis indicator sheet of radiation irradiation of this invention made in order to attain the aforementioned purpose.

[0006] The amount hysteresis indicator sheet of radiation irradiation has the discoloration layer 1 in which the electron donor organic compound of coloration nature and the active species generation organic compound to which coloration of this electron donor organic compound is carried out with a radiation come to contain a hydrophilic compound and a radiosensitizing agent on a part of front face [ at least ] of the base material sheet 2, as shown in <u>drawing 1</u>.

[0007] The amount hysteresis indicator sheet of radiation irradiation may have coloring matter 3 approximated to the hue before discoloration of the discoloration layer 1, and after discoloration at the part on the discoloration layer 1. It can carry out suitably by printing in the ink containing this coloring matter 3. [0008] As shown in drawing 2, as for the discoloration layer 1, it is desirable to be covered with transparence or the translucent protection film layer 4. This protection film layer 4 is for covering ultraviolet rays, for example, mixing or the thing which carried out the laminating is mentioned to polyimide, polyethylene terephthalate or the films made from polypropylene, and these films in an ultraviolet ray absorbent. In order to cover the discoloration layer 1 with the protection film layer 4, it can carry out suitably by preparing and sticking an adhesive layer on the protection film layer 4. The discoloration layer 1 and the base material sheet 2 may be covered by putting by the protection film layer 4 and the adhesive layer.

[0009] The protection film 4 may cover the whole surface of the discoloration layer 1, a part of discoloration layer 1 is put outside, and it may cover it.

[0010] It is desirable to have coloring matter 3 approximated to the hue before discoloration of the discoloration layer 1 and after discoloration in a part of one field of the protection film layers 4. [0011] As the amount hysteresis indicator sheet of radiation irradiation is shown in <u>drawing 3</u>, the base material sheet 2 is transparence or a translucent protection film sheet, and the adhesive layer 6 may be given to the non-observing field of the protection film sheet 2.

[0012] It is desirable that the coloring matter 3 approximated to the hue before discoloration of the discoloration layer 1 and after discoloration is given to a part of one field of the protection film sheets 2. It is for covering ultraviolet rays on the protection film sheet 2, for example, mixing or the thing which carried out the laminating is mentioned to polyimide, polyethylene terephthalate or the films made from polypropylene, and these films in an ultraviolet ray absorbent.

[0013] Another base material sheet 7 may paste the adhesive layer 6.

[0014] As shown in <u>drawing 1</u> and <u>drawing 2</u>, the adhesive layer 5 may be given to the non-observing field of the base material sheet 2. Moreover, as shown in <u>drawing 3</u>, the adhesive layer 8 may be given to the non-observing field of the base material sheet 7. As the quality of the material of adhesive layers 5, 6, and 8, a rubber system binder, a resin system binder, and a silicon system binder are mentioned. The releasing paper may be given to adhesive layers 5, 6, and 8.

[0015] As for a base material sheet, it is desirable that it is the product made of resin or the product made of paper of polyester, polystyrene, and a polycarbonate.

[0016] The amount hysteresis indicator sheet of radiation irradiation is the following, and, specifically, is made and manufactured. The electron donor organic compound 0.01 of coloration nature - 50 weight sections, and the active species generation organic compound 0.1 to which coloration of this electron donor organic compound is carried out with a radiation - 50 weight sections are first mixed to the medium 100 weight section in the hydrophilic compound 0.0001 - 10 weight sections, and the radiosensitizing agent 0.1 which are a radiation absorbent and/or a radiation excitation fluorescence agent - the 100 weight sections. As shown in drawing 1, this is applied to the base material sheet 2, and the discoloration layer 1 is formed. Printing of a pattern 10 obtains the amount hysteresis indicator sheet of radiation irradiation in the ink containing the coloring matter 3 approximated to the hue which the discoloration layer 1 before discoloring on the discoloration layer 1 shows.

[0017] In case radiation treatment is carried out, the amount hysteresis indicator sheet of radiation irradiation is placed near the irradiated object, and if predetermined quantity of radiation is irradiated, it will be discolored. Since it discolors depending on the amount of radiation irradiation, the amount hysteresis indicator sheet of radiation irradiation displays a different hue according to radiation irradiation hysteresis. The predetermined hue which the indicator sheet showed shows that the irradiated object has irradiated the expected dose. The standard color showing a predetermined hue may be attached to the indicator sheet. [0018] Even if it saves the hue from which the discoloration layer 1 changed for a long period of time, it does not fade.

[0019] In addition, the hydrophilic compound of the constituent of the discoloration layer 1 is for controlling fading. A hydrophilic compound has water retention or moistness. A carrageenan, hydroxyethyl cellulose, The macromolecules, ligninsulfonic acid sodium which are chosen from starch and polyvinyl alcohol, Sorbitol, mannite, a maltose, propylene glycol, a glycerol, Alkylamine, a fatty-acid amide, lecithin, and the organic low molecular weight compounds that are chosen from sodium lactate The anionic surfactants chosen from carboxylate, a sulfate salt, a sulfonate, and phosphate The cationic surface active agents. betaine which are chosen from the first class thru/or a quaternary amine salt, An amino carboxylic acid and the amphoteric surface active agents which are chosen from phosphoric ester ammonium salt The polyoxyethylene ether, polyhydric-alcohol partial ester, the polyhydric-alcohol partial ester partial ether, Aliphatic series hydroxy alkylamide and the nonionic surfactants which are chosen from an amine oxide It is desirable that it is at least one kind chosen from either of the inorganic compounds chosen from a potassium pyrophosphate, potassium polyphosphate, sodium metaphosphate, a silicate, and metal hydrate salt. The metal soap represented by a fatty-acid salt and naphthenate as carboxylate among anionic surface active agents is mentioned, the sulfated oil of a glyceride, alkyl sulfate, an alkyl alcoholic sulfate, alkyl ether sulfate, an alkyl ester sulfate salt, and an alkyl aryl ethereal sulfate salt are mentioned as a sulfate salt, an alkyl sulfonate, sulfo succinate, and alkylaryl sulfonates are mentioned as a sulfonate, and alkyl phosphate, alkyl ether phosphate, and alkyl aryl ether phosphate are mentioned as phosphate. As the first class thru/or a tertiary-amine salt, a monoalkyl amine salt, a dialkyl amine salt, and an alkylamine salt are mentioned

among cationic surface active agents, and tetra-alkyl ammonium salt, a benzalkonium salt, alkyl pyridinium salt, and imidazolinium salt are mentioned as a quaternary amine salt. As a betaine, carboxy betaine and sulfobetaine are mentioned among amphoteric surface active agents, and amino acid is mentioned as an amino carboxylic acid. As the polyoxyethylene ether, among nonionic surfactants, polyoxyethylene alkyl ether, Polyoxyethylene alkyl aryl ether and a polyoxyethylene polyoxypropylene glycol are mentioned. As polyhydric-alcohol partial ester, glycerol ester, sorbitan ester, Cane-sugar ester is mentioned. As the polyhydric-alcohol partial ester partial ether The polyoxyethylene ether of glycerol monoester, The polyoxyethylene ether of the sorbitan monoester represented by polyoxy sorbitan mono-URETARATO, The polyoxyethylene ether of sorbitol diester is mentioned and the alkanol amide of a fatty acid and the polyoxyethylene amide of a fatty acid are mentioned as aliphatic series hydroxy alkylamide. The metal hydrate salt among inorganic compounds is BaCl2.2H2O and aluminum2(SO4) 3.14H2O, for example, although it will not be limited especially if it is the metal salt which has water of crystallization. Or aluminum2(SO4) 3.18H2O, CaSO4.2H2O, and NiSO4.7H2O are mentioned. [0020] It is desirable that it is at least one kind as which the electron donor organic compound of coloration nature is chosen from triphenylmethane color phthalides, fluoran, phenothiazins, indolyl phthalides, leuco auramine, rhodamine lactams, rhodamine lactone, indoline, and thoria reel methane. As triphenylmethane color phthalides, crystal violet lactone, As Malachite Green lactone and fluoran, 3-diethylamino benzoalpha-fluoran, 3-diethylamino-7-chlorofluoran, 3-diethylamino-7-dibenzylamino fluoran, As 3, 6-dimethoxy fluoran, and phenothiazins, 3, 7-bisdimethyl amino-10-(4'-amino benzoyl) phenothiazin, As indolyl phthalides, 3 and 3-bis(1-ethyl-2-methylindole-3-IRU) phthalide, 3 and 3-bis(1-n-butyl-2-methylindole-3-IRU) phthalide, As leuco auramine, N-(2, 3-dichlorophenyl) leuco auramine, As N-phenyl auramine and rhodamine lactams, a rhodamine-beta-o-chloro amino lactam, As rhodamine lactone, as rhodamine-betalactone and indoline, 2-(phenyl iminoethane zylidene)-3 and 3'-dimethylindoline, As p-nitrobenzyl leuco methylene blue, benzoyl leuco methylene blue, and thoria reel methane, a bis(4-diethylamino-2methylphenyl) phenylmethane and tris (4-diethylamino-2-methylphenyl) methane are mentioned. The electron donor organic compound of this coloration nature is usually colorlessness or light color, and has active species, i.e., the property colored in an operation of an electron acceptor, such as Broensted acid and Lewis acid. If a radiation is irradiated, active species produces an active species generation organic compound irreversibly, it is desirable that it is the compound which has a halogen radical, and, specifically, carbon tetrabromide, the tribromoethanol, and tribromonethyl phenylsulfone are mentioned. As for a radiosensitizer, it is desirable that it is at least one kind of radiation absorbent chosen from the metal of barium, an yttrium, silver, tin, a hafnium, a tungsten, platinum, gold, lead, a bismuth, a zirconium, and a europium and the compound containing this metal, and, as for the compound containing a metal, a sulfate, a carbonate, and a nitrate are mentioned. The salt a radiosensitizing agent is indicated to be by CaWO4, MgWO4, and HfP207, ZnS:Ag, ZnCdS:Ag, CsI:Na, CsI:Tl, BaSO4:Eu2+, Gd2O2S:Tb3+, La2O2S:Tb3+, La2O2S:Tb3+, You may be at least one kind of radiation excitation fluorescence agent chosen from the baking object shown by Y2O2S:Tb3+, Y2SiO5:Ce, LaOBr:Tm3+, BaFCl:Eu2+, and BaFBr:Eu2+. The baking object of ZnS: Ag uses zinc sulfide as a principal component, and adds and calcinates the silver which is a heavy-metal activator. Other baking objects are obtained similarly.

[0021] For example, an ink vehicle is mentioned to a medium.

[0022] Although it is unknown that this indicator sheet's fading is controlled for details, it is imagined as what is depended on the following mechanisms. If a radiation is first irradiated by the indicator sheet, the radiosensitizing agents in a discoloration layer will be absorbed and scattered about in a radiation, and the active species from a lifting and an active species generation organic compound will be generated in the photoelectric effect, the Compton effect, the phenomenon of the electron pair production which emitted the electron, and fluorescence phosphorescence luminescence. Since active species has electronic receptiveness, the charge transfer of the electron donor organic compound of the intermingled coloration nature is induced. Then, since the electron density changes, coloration of the electron donor organic compound is carried out, and thereby, an indicator sheet discolors it. It will not fade, in order for the electron acceptor of the hydrogen ion produced by the radiation irradiation to the hydrophilic compound which lives together, or its content moisture to stabilize the electron donor organic compound which carried out coloration. Therefore, it can save by the hue [ having discolored this indicator sheet ] for a long period of time.

[0023] This indicator sheet can display the wide range dose of 5Gy - 25,000Gy. In addition, accommodation of the hue after discoloration, the shade of a color, and a discoloration rate is possible by adjusting the class and compounding ratio of the above-mentioned matter which compose a discoloration layer according to the amount of radiation irradiation which should manage an irradiated object.

[0024]

[Embodiment of the Invention] Hereafter, the example of this invention is explained to a detail. <u>Drawing 1</u> is a cross section showing the example of the amount hysteresis indicator sheet of radiation irradiation which applies this invention. The amount hysteresis indicator sheet of radiation irradiation has the discoloration layer 1 which the indolyl phthalides which are the electron donor organic compound of coloration nature, the carbon tetrabromide which is an active species generation organic compound, the carrageenan which is a hydrophilic compound, and the barium sulfate which is a radiosensitizer become from the constituent currently mixed by the medium on the front face of the base material sheet made from plastics, as shown in <u>drawing 1</u>. On the discoloration layer 1, the pattern and the alphabetic character are printed in the ink containing the hue of the discoloration layer 1, and the coloring matter 3 to approximate. As shown in <u>drawing 4</u> (a), the hue approximates the printing part 10 and the non-printed part 11 of a pattern. The non-observing field of the base material sheet 2 has the adhesive layer 5.

[0025] In the case of radiation irradiation, this indicator sheet is stuck on an irradiated object, and a radiation, for example, an X-ray, or a gamma ray is irradiated. An indicator sheet is taken out when an exposure is completed. The condition of the indicator sheet at this time is shown in <u>drawing 4</u> (b). Although the discoloration layer 1 carries out coloration by the exposure of a radiation, in the pattern printing part 10.

radiation, for example, an X-ray, or a gamma ray is irradiated. An indicator sheet is taken out when an exposure is completed. The condition of the indicator sheet at this time is shown in <u>drawing 4</u> (b). Although the discoloration layer 1 carries out coloration by the exposure of a radiation, in the pattern printing part 10, only the hue of ink is observed, and as a result of observing the hue which the discoloration layer 1 discolored, on the other hand in the non-printed part 11, the pattern printing part 10 appears as an extraction pattern. Thereby, it can be checked that predetermined radiant quantities have been irradiated. Since the indicator sheet after discoloration does not fade, prolonged preservation can be performed as a proof which shows that the predetermined dose has been irradiated with the hue after discoloration.

[0026] In addition, the indicator sheet may be printing the extraction pattern in the ink containing the coloring matter 3 approximated to the hue after discoloration of a discoloration layer as shown in <u>drawing 5</u> (c). Before radiation irradiation, since, as for the pattern printing part 20 and the non-printed part 21, the hue is different, the non-printed part 21 has appeared as an extraction pattern. If a radiation is irradiated at this indicator sheet, as shown in <u>drawing 5</u> (d), since the hue from which the discoloration layer 1 changed is observed and the hue of the pattern printing part 20 is resembled, an extraction pattern will disappear in the non-printed part 21.

[0027] Below, the example which made the amount hysteresis indicator sheet of radiation irradiation of this invention as an experiment is explained.

[0028] After stirring the carrageenan 0.5 weight section underwater as the barium-sulfate 10 weight section and a hydrophilic compound as an absorption-of-radiation agent, moisture was volatilized and the mixture of an absorption-of-radiation agent and a hydrophilic compound was produced. The carbon tetrabromide 10 weight section was mixed with this as an electron donor organic compound of coloration nature as the purga script red I-6B(Ciba Specialty Chemicals make) 10 weight section which are indolyl phthalides, and a radiation activator, the ink vehicle (PAS-800 ink medium: Product made from 10 \*\*\*\*\*\*) 100 weight section was mixed as a medium, it considered as the constituent, this was applied to the base material sheet made from a polyethylene film, and the indicator sheet was obtained.

[0029] The 15Gy X-ray was irradiated by X-ray irradiation equipment MBR-1520A-2 (Hitachi Medical [Corp.] Corp. make), and when the indicator sheet was taken out on this indicator sheet and it observed on it by viewing, red was shown in it. After saving the indicator sheet furthermore irradiated for three weeks within 40-degree-C thermostat, when it observed similarly, the hue just behind X-ray irradiation and this appearance were \*\*\*\*\*(ed). Moreover, the same result was obtained, when it replaced with the X-ray and the gamma ray by the gamma ray irradiation equipment gamma cel 1000 elite (product made from MDS Nordion) was irradiated at the indicator sheet.

[0030] In addition, the indicator sheet may have the adhesive layer by which the releasing paper was given to the non-observing field of a base material sheet. A releasing paper may be removed and you may stick on an object.

[0031]

[Effect of the Invention] As mentioned above, a radiation control person can check that the dose has been suitable in the case of radiation irradiation processing of transfusion blood and a medical supply by using the amount hysteresis indicator sheet of radiation irradiation of this invention, as explained to the detail. Discoloring an indicator sheet clearly by radiation irradiation, the hue does not fade for a long period of time. Therefore, an indicator sheet can perform prolonged preservation as a proof which shows that the predetermined dose has been irradiated.

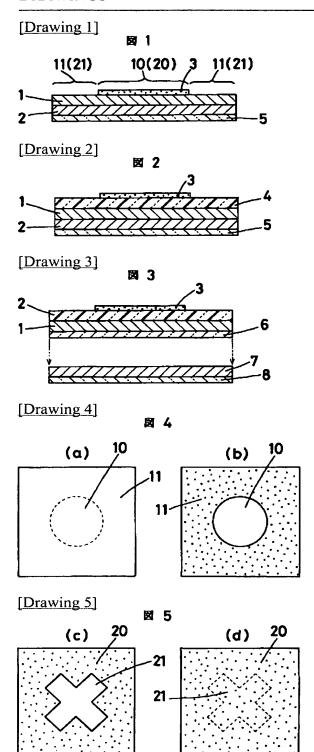
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## **DRAWINGS**



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